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CEYLON RUBBER RESEARCH COMMITTEE.

REPORT ON THE DETERMINATION OF THE PLASTICITY OF RUBBER.

REPORT ON THE EFFECT OF DILUTING LATEX ON THE PLASTICITY OF CREPE.

REPORT ON THE EFFECT OF ORGANIC ACCELERATORS OF VULCANISATION ON THE VARIABILITY OF RUBBER.

CONTRIBUTIONS FROM THE RUBBER RESEARCH SCHEME, CEYLON.

CEYLON RUBBER RESEARCH COMMITTEE.

REPORT ON THE POSSIBILITY OF LATEX BECOMING CONTAMINATED WITH BORDEAUX MIXTURE AS A RESULT OF SPRAYING OPERATIONS.

PREVIOUS investigations (Quarterly Circular No. 4, 1926) have shown that Bordeaux mixture in latex causes the raw rubber to become tacky on keeping and the vulcanised rubber to perish quickly. Although great care is taken on estates to spray only the crowns of trees there is a risk of heavy rains washing the Bordeaux mixture on to the tapping cuts (Quarterly Circular No. 2, 1927). It is stated that in Southern India where spraying operations are carried out on an extensive scale there is no instance of the rubber becoming tacky. On the other hand a trace of Bordeaux mixture, sufficient to cause serious deterioration in the vulcanised product, would not be detected by the appearance of the raw rubber unless it had been kept for some considerable time.

At the request of the Ceylon Committee five samples of machine-dried crepe were accordingly obtained from Southern India by Mr. Bertrand in order that the question might be further investigated. The only information supplied concerning their preparation was that they were "made from latex from a field which is being sprayed with Bordeaux mixture" and that "the rubber sent was from blocks being tapped *at the time of spraying*. No rain fell during the time. Age of trees 21 years. The rubber was machine-dried."

The samples were forwarded to the Imperial Institute for examination, where the raw rubber was submitted to plasticity tests and the vulcanised product to artificial ageing tests. Details of the results are given below, from which it will be seen that the keeping properties are satisfactory in all cases. It should be noted however, that the samples were prepared during fine weather when there was the least risk of Bordeaux mixture reaching the tapping cut.

Although in no case has it been established that spraying the crowns of the trees with Bordeaux mixture either in Ceylon or in Southern India introduces sufficient copper into the latex to cause marked deterioration of the raw or vulcanised rubber, it cannot be too strongly emphasised that its use requires the greatest care.

(A) PLASTICITY TESTS.

Sample No.	Raw Rubber.		Masticated Rubber.	
	D30*	Time of Mastication.	D30*	Ev+
	(mm./100)	(mins.)	(mm./100)	(ccs.).
1327	140	21½	76	11·7
1328	144	22½	73	13·8
1329	139	22	71	14·1
1330	146	22½	73	13·7
1331	145	24	74	13·5

*D30= Thickness (in hundredths of a millimetre) of sphere 0·4 grams in weight after pressing in parallel plate plastimeter at 100°C for 30 minutes.

+Ev= Volume in ccs. extruded in 1 hour at 90°C.

These results show that the samples, although more plastic than air-dried crepe, are not definitely more plastic than average machine-dried crepe, and much less plastic than the set of samples previously examined which were prepared from latex to which small quantities of Bordeaux mixture were added.

(B) ARTIFICIAL AGEING TESTS.

The samples were vulcanised in a rubber-sulphur mixing (90·10) at 148°C and submitted to artificial ageing tests in a current of air at 70°C.

Sample No.	Time of vulcanisation.	Period of ageing.	Tensile Strength.	Elongation	
				At Break.	At load of 1·04 kgs./sq.mm.
	(mins.)	(hrs.)	(lbs./sq. in.)	(per cent.)	(per cent.)
1327	120	nil	1870	908	850
		48	2130	827	755
		96	1460	736	735
		144	990	583	675
1328	114	nil	1810	935	877
		48	2250	873	786
		96	1920	784	727
		144	890	564	723
1329	116	nil	1830	913	870
		48	2100	876	806
		96	1910	802	741
		144	840	581	700
1330	125	nil	1840	885	846
		48	2120	833	754
		96	1850	767	706
		144	370	412	—
1331	125	nil	1990	907	854
		48	2050	818	752
		96	1830	774	709
		144	400	426	—

These samples vulcanise somewhat more slowly than machine-dried crepes from a number of Ceylon estates. The artificial ageing properties are similar to those usually found for crepe.

It may be concluded from this investigation that none of the samples contains even a trace of Bordeaux mixture.

Imperial Institute,
London, S.W.
June, 1928.

REPORT ON THE DETERMINATION OF THE PLASTICITY OF RUBBER.

IT is generally agreed that the consistency of raw and masticated rubber is of considerable importance and requires detailed study, but it is only recently that definite methods of measurement have been devised. Previous to the introduction of these tests a technologist pulled and pressed a piece of rubber between his fingers and described it as hard, soft, plastic, tough, nervy, weak, short, etc., according to his conception of the meaning of the terms and the impression he had formed of the material under examination. No investigation is likely to be successful which lays its foundation on these shifting sands of vague terms and personal opinions. Attempts have therefore been made by several investigators to find a more satisfactory basis of study.

Two main types of test have now been developed, viz:—an extrusion and a compression test. In the extrusion test (introduced by Marzetti) the rubber is deformed by forcing it at a definite temperature and pressure through a small orifice. The rate at which the rubber flows is regarded as a messure of plasticity. In the compression test introduced by Ira Williams a small ball of rubber is pressed by a weight and the rate at which the rubber decreases in thickness is regarded as a measure of plasticity. Each of these methods is used by different manufacturers who state that the results obtained agree with works experience. Neither method can be regarded as wholly satisfactory however because the results are largely dependent upon conditions. This is particularly noticeable in the case of extrusion tests as shown in the following paragraphs:—

Extrusion Tests.—An experiment was carried out at the Imperial Institute in which a series of samples of crepe was extruded under high and low pressures through the same orifice. The following are the results obtained:—

Sample No.	Rate of Extrusion.	
	Load 165 lbs./sq. in.	Load 1,000 lbs./sq. in.
1380	25·6	28·6
1381	23·8	27·5
1382	15·4	26·6
1383	14·9	24·8
1384	14·5	24·8

There is considerable difference between the rates of extrusion of sample 1380-1 and of samples 1382-4 at the low loads but not at the high loads.

Other experiments show that the relation between the results of tests on different samples not only changes with the loads but also with the dimensions of the orifice.

The effect of load on rate of extrusion was studied in detail at the Imperial Institute for a large number of samples of masticated rubber. It was found that the character of the flow altered with the load applied. At low loads evidence was obtained which suggested that the flow of the rubber was not wholly telescopic, i.e., the flow measured was a combination of plastic and other types of flow. At higher loads there was definite evidence of slipping at the walls of the orifice. The differences in the character of the flow as the load was increased was confirmed by the change in the appearance of the extruded "worm." At the lowest load tried the "worm" was always smooth. On increasing the load it became corrugated. At higher loads still it became smooth again but developed a spiral twist which was very marked at the highest loads tried.

When the diameter of the orifice was considerably reduced and its length increased the mathematical relation between load and rate of extrusion was different from that obtained previously. There was no definite evidence of slipping at the walls of the orifice and it is considered that the flow was more in accord with true plastic flow. This question is still under consideration and it is hoped to deal with it in a later publication.

Although rate of extrusion depends upon too many factors to form a sound basis for the comparison of plasticities, there is no doubt that as a rough test it is a valuable help. For example no difficulty is experienced in following the increase in plasticity of rubber during mastication, and at the Imperial Institute advantage is taken of this fact to study the effect of mastication on rubber.

It is considered that the plasticity of the unmasticated rubber is of little practical importance compared with the rate at which the plasticity of the rubber increases during mastication. The rubber is therefore ground through laboratory rolls for different times and the number of grindings required to reduce the rubber to a condition in which it extrudes at a fixed rate is determined. Small differences between different rubbers cannot be detected with certainty by this method, but if attention is concentrated on large differences there is little doubt that the tests are of considerable value.

Compression Tests.—Concurrently with the investigation of the fundamental principles underlying the extrusion test, a similar study has been made of the compression test. Considerable progress has been made enabling these tests to be placed on a much sounder basis than previously.

The simplest form of the compression test is that introduced by Van Rossem and Van der Meyden, the rubber under test being placed on a raised platform so that there is a constant area of rubber in contact with the weight, instead of an area which increases as the thickness decreases. Under these conditions it was found at the Imperial Institute that there is a simple and accurate relation between the thickness of the rubber and the rate at which it decreases in thickness. This relation is expressed by the equation

$$\frac{1}{S_2^2} - \frac{1}{S_1^2} = Kt.$$

where S_1 and S_2 represent initial and final thickness over the time interval t. The value of K depends upon the plasticity of the rubber and the conditions of the experiment, but it is constant throughout an experiment.

The question has also been studied theoretically with a view to obtaining measurements in absolute units, and at the request of the Imperial Institute considerable help has been given by the staff of the National Physical Laboratory. The problem is comparatively simple for a viscous liquid but is much more complex for a plastic solid, and further work on fundamental principles is necessary. It is hoped to carry out this work when opportunity arises.

The results already obtained however are of considerable practical value because they enable the relative plasticities of different rubbers to be obtained in a quick test with simple apparatus in units which are theoretically proportional to the rate of extrusion and therefore very sensitive to changes in plasticity. The test has the further advantage that different laboratories in different parts of the world should have no difficulty in obtaining the same results with rubber of the same plasticity. In the case of extrusion tests this would be difficult to achieve. It is considered premature however to put forward definite suggestions at present as the work is still proceeding, practical details require consideration, and further improvements may shortly be made.

Imperial Institute,
London, S.W., 7.
February, 1929.

REPORT ON THE EFFECT OF DILUTING LATEX ON THE PLASTICITY OF CREPE.

THE results of the examination of a previous series of samples prepared in Ceylon at the request of the London Committee indicated that crepe prepared from diluted latex is more plastic than that from undiluted latex, as determined by tests on the raw rubber. Tests on the masticated rubber however did not show a regular change with dilution (Bulletin No. 49).

A further set of samples has now been examined consisting of crepe prepared from undiluted latex (34·7 per cent. dry rubber) and from the same latex diluted to 30, 20, 10 and 5 per cent. dry rubber. As in the case of the previous set no bisulphite was added and the amount of acetic acid used for coagulation was adjusted to the dilution of the latex.

The following are the results of plasticity tests:—

TABLE I.

Plasticity tests.

Sample No.	Concentration of latex.	Raw rubber D_{30}+	Number of grindings through laboratory rolls required to reduce rubber to a standard plasticity.*
	per cent. dry rubber.	mms./100	
1380	35	166	64
1381	30	168	60
1382	20	163	60
1383	10	160	60
1384	5	154	55

* The standard of plasticity adopted is a rate of extrusion of 10 cc. per minute under load of 1000 lb./sq. in. at 85°C.

+D_{30} = Thickness (in hundredths of a millimetre) of sphere 0·4 grams in weight after pressing in plasticity press at 100°C for 30 minutes.

The results of tests on the raw rubber are very similar to those given by the previous set of samples. On the whole the more dilute the latex the more plastic is the rubber obtained from it.

Experiments in Java by Dr. de Vries indicate that there is little difference in the plasticity of crepe from diluted and undiluted latex when first prepared but that the plasticity of the crepe from diluted latex increases more than that from undiluted latex on keeping for 12 months in the tropics (Archief voor de Rubber-

cultuur April 1928, p. 259). The results obtained in Java are consistent with those found at the Imperial Institute where the samples are tested six months after arrival, i.e., about eight months after preparation.

The results obtained at the Central Rubber Station, Java, and the Imperial Institute are compared in the following table:—

TABLE II.

Ceylon Rubber Research Scheme Tests in London 8 months after preparation.						Central Rubber Station Tests in Java*		
Sample No.	Concentration of latex.	D_{30}	Sample No.	Concentration of latex.	D_{30}	D_{30}		
						Dilution	Fresh rubber.	Rubber one year old.
	per cent. dry rubber.	mm./100		per cent. dry rubber.	mm./100		mm./100	mm./100
1355	35	167	1380	35	166	1·1	1·55	1·43
1356	30	165	1381	30	168	1·4	1·55	1·38
1357	20	160	1382	20	163	1·9	1·51	1·31
1358	10	159	1383	10	160	1·49	1·48	1·20
1359	5	156	1384	5	154			

* See Transactions of the Institution of the Rubber Industry, III 1927, p. 293.

All these experiments support the view that a few months after preparation raw crepe from diluted latex is softer than that from the undiluted latex.

Mastication experiments on laboratory mixing rolls indicate however that in the case of both series of crepes from Ceylon the change in plasticity of the raw rubber is of little practical importance. For example in the previous series of experiments carried out in London (Bulletin 49) in which the rubber was masticated until it had consumed a fixed amount of power, the differences in the rate of extrusion were irregular and small. In the tests on the present series (see Table I) the samples were ground through the rolls a fixed number of times and the amount of mastication to produce a fixed rate of extrusion calculated. The differences were again small, but the crepe from the very dilute latex required less mastification than that from undiluted latex.

It seems probable from these experiments that several months after preparation, raw crepe from very dilute latex would be softer than crepe from undilted latex, but there would be little difference in the amount of mastication required to render the rubber sufficiently soft for factory operations. On the whole the crepe from the very dilute latex would require the least mastication.

Imperial Institute,
London,
November, 1928.

REPORT ON THE EFFECT OF ORGANIC ACCELERATORS OF VULCANISATION ON THE VARIABILITY OF RUBBER.

THE vulcanising properties of rubber are usually determined by mixing in sulphur and determining the period of heating at 140-150°C required to produce optimum mechanical properties. This period varies with the sample under examination.

A vulcanised mixture of rubber and sulphur is too soft for most commercial applications, and it is necessary to add other substances, many of which have a considerable effect on the mechanical properties of the vulcanised material. Some also have a marked effect on the time required for vulcanisation. The most important of these latter substances are organic accelerators which are now extensively used to aid vulcanisation and to improve the mechanical properties of the vulcanised product. It has been the practice therefore at the Imperial Institute not only to determine the vulcanising properties of rubber in a rubber-sulphur mixing but also in one containing an organic accelerator and zinc oxide, the latter being necessary for the activation of many organic accelerators.

The comparison between the results of tests in a rubber-sulphur and an organic accelerator mixing is complicated by an important difference as regards the behaviour of the two types of mixing on vulcanisation. Whereas the mechanical properties of a rubber-sulphur mixing change rapidly with the period of vulcanisation, those of an accelerator mixing remain fairly constant for a long period. Consequently in the case of the rubber-sulphur mixing the variation between different samples of rubber can be defined in terms of the time of vulcanisation, but in the case of the accelerator mixing comparisons have to be made as to the ability or inability of samples to attain certain mechanical properties.

The basic mixing used throughout these investigations consisted of rubber, sulphur, zinc-oxide and an organic accelerator. The proportion of each constituent, except that of zinc oxide, is in practice fixed within certain narrow limits depending upon a number of factors. The amount of zinc-oxide however can be varied from the few per cent. necessary to activate the accelerator to an amount in excess of the weight of rubber present. The first experiments at the Imperial Institute (J.S.C.I., 1923, *42*, 98) were made with accelerator mixings containing about 5 per cent. of zinc-oxide on the rubber, and with samples of rubber which had been in stock for several years. Under these conditions remarakable variations in the behaviour

of the different samples was observed. Some of them scarcely vulcanised no matter how long the period of vulcanisation, whilst others had excellent mechanical properties after a very short period of vulcanisation. Further experiments showed however that this variation was confined to accelerator mixings containing about 5 per cent. zinc-oxide. When the amount of zinc-oxide was increased considerable so that equal quantities of zinc-oxide and rubber were present, the differences disappeared.

The variation in the behaviour of samples in the presence of 5 per cent. zinc-oxide was traced to differences in the accessory substances naturally present in rubber. When some of these accessory substances were removed by extraction with acetone, samples which previously vulcanised well in the presence of 5 per cent. zinc-oxide and an organic accelerator no longer vulcanised satisfactorily. When the extracted accessory substances were added back to the rubber during mixing, vulcanisation was again satisfactory.

These results were subsequently confirmed by Sebrell and Vogt (Ind. Eng. Chem., 1924, *16*, 792) who also showed that the important accessory substances were the fatty acids which Whitby (J.S.C.I., 1923, *42*, 336T) had previously shown were present to the extent of over 1 per cent. in most samples of rubber. The experiments of Sebrell and Vogt however were confined to mixings containing about 5 per cent. zinc-oxide. The experiments at the Imperial Institute show that fatty acids are not a source of variation in the presence of large quantities of zinc-oxide. Whitby (J.S.C.I., 1928, *18*, 122T) has recently challenged this conclusion but further experiments, the results of which will shortly be published, confirm its validity.

The remarkable effect of fatty acids in mixings containing 5 per cent. zinc-oxide is considered to be due to a better distribution of the zinc-oxide in the presence of fatty acids. The zinc-oxide is not dissolved in the rubber but is present as separate discrete particles. Most accelerators require a minimum amount of zinc-oxide to reach full activity. The distribution of the zinc-oxide is therefore of considerable importance when only small quantities are present.

The question remains as to the extent of the variability in first grade rubber when vulcanised in accelerator mixings containing 5 per cent. zinc-oxide and an organic accelerator. It has already been pointed out that the samples which displayed so much variation were several years old at the time of the tests and therefore not representative of the crepe and sheet usually employed in the factory. It was subsequently shown by Whitby (Trans I.R.I., 1924, *1*, 12) that the amount of fatty acids in rubber tends to become very small on keeping. It is to be expected therefore that these samples would be variable in the mixing chosen.

Tests were therefore carried out on 39 samples not more than two years old collected from estates, and on others six months old specially prepared by methods known to have a considerable effect on the rate of vulcanisation in a rubber-sulphur mixing. The mixings tried were:—

	(a)	(b)
Rubber	90	90
Sulphur	5	5
Zinc-oxide	5	5
Accelerator	1 hexamethylene tetramine.	1 diphenylguanidine

No variation of importance was observed with the above samples, although both mixings gave unsatisfactory results in the absence of fatty acids. It may be concluded therefore that there are sufficient fatty acids in crepe and sheet (for the first two years after preparation) to prevent marked fluctuations in vulcanising properties in the presence of organic accelerators and 5 per cent. zinc-oxide.

Since it has already been shown that fatty acids do not cause appreciable variability in the presence of larger quantities of zinc-oxide, it might be concluded that accelerators completely eliminate variability in first grade rubber. The results of a large number of experiments by Dinsmore and Zimmerman (Ind. Eng. Chem., **1926**, *18*, **144**) however do not confirm this conclusion. A few tests were therefore carried out at the Imperial Institute using one of the mixings employed by the above investigators, and it was found that the accelerator mixings employed by them did not eliminate variability.

The only difference between the accelerator mixings which displayed some variability and those which did not was in the proportion of accelerator and sulphur to the rubber. A study of the effect on variability of the sulphur accelerator ratio had not previously been made, but it is evident from the following results on two estate samples selected at random that it is of considerable importance.

	Addition to 100 parts of rubber.				Sample No. 1215.		Sample No. 1225.	
Mix	Zinc Oxide	Sulphur.	Diphenyl-guanidine.	Time of vulcanisation at 148° C.	Tensile Strength	Elongation at load of 104 kgs./sq m m.	Tensile Strength.	Elongation at load of 104 kgs./sq. m.m.
	(parts)	(parts)	(parts)	(mins.)	(lbs./sq. in.)	(per cent.)	(lbs./sq. in.)	(per cent.)
1	nil	11·1	nil	100	1150	905	1910	873
2	6·0	2·75	0·4	20	590	—	1250	1035
				30	680	—	1790	931
				40	1010	935	1750	877
3	6·0	5·5	0·4	20	1200	870	1900	861
				30	1550	820	1980	759
				40	1830	754	2140	694
4	5·6	5·6	1·1	25	2880	573	2990	580

In the rubber-sulphur mixing (Mix. 1) samples 1215 required about 10 per cent. longer period of vulcanisation to give the same mechanical properties as sample 1225.

On vulcanising in Dinsmore and Zimmerman's mixing (Mix. 2) the presence of the accelerator and zinc-oxide has increased the difference between the two rubbers. When the amount of sulphur in this mixings is doubled (Mix. 3) there is less difference between the samples, and when the amount of accelerator is also increased (Mix. 4—Imperial Institute routine mix.) the difference between the two samples is negligible.

It is evident therefore that the difference between Dinsmore and Zimmerman's results and those obtained at the Imperial Institute is due to the fact that the former employed much lower proportions of sulphur and accelerator in their mixing.

The proportion of sulphur to accelerator is of considerable importance in manufacturing practice and many manufacturers reduce the amount of sulphur as much as is consistent with satisfactory mechanical properties. A critical ratio can be obtained for an accelerator (Schidrowitz and Burnand J.S.C.I., 1921, *40*, 268T) below which it is not good practice to reduce the amount of sulphur present. It seems likely from the above experiments that this critical ratio varies with the rubber. The question has not yet been studied extensively but there is some evidence that the serum substances are the cause of this variability.

The experiments with the mixings employed at the Imperial Institute indicate that all variability in first grade rubber can be avoided by using suitable proportions of sulphur and accelerator. There are other and more important considerations however which affect a manufacturer's choice of a mixing for any purpose, and it is understood from several independent enquiries that the mixings employed by Dinsmore and Zimmerman may be regarded as typical of manufacturing practice. With these mixings there is a certain amount of variability, but there is no evidence that wide variations are liable to occur such as are sometimes experienced in a rubber-sulphur mixing.

Imperial Institute,
London, S.W., 7.
February, 1929.

NOTICES.

SUBSCRIPTIONS.

Arrangements have now been made for Bulletins of the Ceylon Rubber Research Scheme to be made available to non-contributors to the Scheme at the rate of Rs. 15-00 per annum, post free.

OFF-COLOURED CREPE.

The Chemist to the Rubber Research Scheme would be glad to get into touch with the Superintendent of any estate who is troubled with off-colour crepe, and who thinks that this may be due to impurities in the water used for manufacture.

GLASS METROLOCS.

Glass Hydrometers for testing latex as specified and as recommended by the Rubber Research Scheme (Ceylon) may be obtained at a cost of Rs. 12-50 each from :—

Messrs. WALKER, SONS & Co., Ltd.,
Engineering & Estate Supplies Department,
Colombo.